

DISPOSAL OF SWEET CHERRY PROCESSING BRINES

ABSTRACT

Alternative procedures for the disposal of waste calcium bisulfite cherry processing brine were investigated. SO_2 concentrations in waste brine can be reduced to several hundred ppm by neutralization with lime and filtration or sedimentation to separate precipitated CaSO_3 . Lower SO_2 concentrations can be achieved by oxidation with H_2O_2 . Anaerobic storage of sludge and supernatant from neutralized brine may produce objectionable odors. Brine to be disposed in deep wells should be pretreated by neutralization and sedimentation. Substitution of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ for CaCl_2 in brine formulations to eliminate chloride from processing waste was not feasible.

INTRODUCTION

THE DISPOSAL OF WASTE calcium bisulfite brines used in sweet cherry processing represents a serious problem for this industry. Such brines represent a source of air and water pollution and are difficult to treat. This problem may be alleviated in part by the reuse of waste brine after filtration and treatment with activated carbon (Beavers et al. 1970; Soderquist, 1971; Panasiuk et al. 1977). However, some brine may not be suitable for reclamation because of poor quality (contamination with iron or low strength) or economic constraints (low volume or high collection and shipping costs) and presents a continuing disposal problem.

We have investigated several alternative strategies for the disposal of cherry processing brine and problems associated with these procedures. Described herein are the results of our studies of brine neutralization and calcium sulfite precipitation, the anaerobic degradation of neutralized brine, the oxidation of residual SO_2 with H_2O_2 , deep well disposal, and brine reformulation with calcium dihydrogen phosphate.

MATERIALS & METHODS

Brine formulations

All waste brines used in disposal experiments were dry mix formulations that had been used to brine Windsor cherries during the 1973 and 1974 seasons in Michigan.

Simulated waste brines, used to determine the effects of organic acids on calcium sulfite precipitation, contained 0.406% calcium bisulfite (2500 ppm SO_2), 1.0% calcium chloride (anhyd), and either 0.32% fumaric acid, 0.36% citric acid monohydrate, or 0.30% malic acid.

Dry mix formulations, used to compare titrimetric and specific ion electrode procedures for the determination of calcium, contained 2.32% sodium bisulfite, 1.99% calcium chloride (anhyd), and either 0.305% fumaric acid or 0.375% citric acid monohydrate.

Brines containing calcium dihydrogen phosphate in place of calcium chloride were prepared using the following formulation: 2.30% sodium bisulfite, 0.565% citric acid monohydrate, and either 2.97% (5000 ppm Ca) or 4.70% (8000 ppm Ca) calcium dihydrogen phosphate monohydrate (reagent grade).

Precipitation of calcium sulfite

Brine samples were neutralized by the gradual addition of measured quantities of $\text{Ca}(\text{OH})_2$ or other bases, with stirring, until the desired pH was attained. In timed experiments, the addition time was varied from 2 to 10 min. After neutralization, the brine was held for approximately 10 min and then filtered through Whatman No. 2 filter paper, yielding a sparkling clear filtrate. The filtrate was analyzed for residual SO_2 .

Sedimentation was investigated as an alternative to filtration for the separation of calcium sulfite from neutralized brine. After neutralization, the brine-calcium sulfite suspension was transferred to a 250-ml separatory funnel and held for 5 min to permit settling. The sediment layer (with some supernatant) was quantitatively transferred by draining into a 100-ml graduated cylinder and redispersed by inverting the stoppered cylinder once. Sedimentation in the cylinder was then timed, and the volume of the sediment layer was recorded after 2, 5, 10 and 15 min.

Anaerobic fermentation of neutralized brine

A model system was devised to simulate the decomposition of neutralized waste brine and calcium sulfite sludge during storage in anaerobic lagoons and landfills. Brine and sludge samples were placed in 4-oz screw cap bottles (filled to the top), inoculated with a mixed culture of microorganisms (in garden soil), tightly closed to exclude air, and incubated for 4–5 days at room temperature. Bottles were observed for turbidity, gas formation, and odor during incubation.

Experiments were carried out with the sludge and supernatant from a neutralized strong brine and with sludge that had been washed with H_2O in a coarse sintered glass funnel to remove sugars and other dissolved solids present in the adhering brine. Additional experiments were carried out with weak brines that had undergone oxidation during storage, converting essentially all of the bisulfite to bisulfate. These brines were neutralized and then filtered through Whatman No. 2 filter paper to separate the precipitate calcium sulfate.

Oxidation of neutralized brine with H_2O_2

Neutralized waste brine was filtered through Whatman No. 2 filter paper to remove precipitated calcium sulfite. H_2O_2 (31.8%, diluted 1:20) solution was added at different levels to 100 ml portions of brine filtrate, and aliquots were taken for SO_2 analysis after 5 and 60 min.

Analytical methods

SO_2 was determined by iodometric titration and calcium by EDTA titration, as described by Payne et al. (1969). Calcium activity was measured with an Orion 92-20 specific ion electrode, using the procedure described in the instruction manual (Orion Research, Cambridge, MA 02139).

RESULTS & DISCUSSION

Precipitation of sulfite and sulfate

Bisulfite and the bisulfate that arises from oxidation during storage ($2\text{HSO}_3^- + \text{O}_2 = 2\text{HSO}_4^-$) represent key elements of the brine disposal problem since these components are precursors of objectionable odors, may disrupt biological treatment systems, and may lower waste-water pH enough to damage sewer lines and treatment facilities (Beavers et al., 1970). We have investigated the removal of residual bisulfite and bisulfate from waste brine by neutralization and precipitation with calcium ($\text{HSO}_3^- + \text{OH}^- = \text{SO}_3^{2-} + \text{H}_2\text{O}$; $\text{Ca}^{++} + \text{SO}_3^{2-} = \text{CaSO}_3$). According to Payne et al. (1969) the conversion of bisulfite to sulfite is virtually complete above pH 7–8. New cherry brine contains approximately equimolar concentrations of calcium and bisulfite while used brine contains a molar excess of calcium since some bisulfite is lost as SO_2 gas or by oxidation. Consequently, neutralization of used brine will result in the precipitation of calcium sulfite and calcium sulfate.

Data summarized in Table 1 show the effect of neutralizing a used brine sample with calcium hydroxide, an inexpensive alkali that is easy to handle and also provides additional cal-

cium, which promotes precipitation. The neutralized brine, after filtration to remove the calcium sulfite precipitate, was found to contain almost 400 ppm SO₂, even when the pH was increased to 9. The maximum level of Ca(OH)₂ addition represents approximately 140% of the amount theoretically required for the neutralization of bisulfite. Presumably, some Ca(OH)₂ is used to neutralize organic acids and bisulfate. Similar results have been obtained with other used brines; the Ca(OH)₂ requirement varies with the SO₂ concentration of the brine.

The relatively high residual SO₂ concentration in neutralized used brine probably is due to the presence of organic acids which chelate calcium and interfere with calcium sulfite precipitation. The effect of fumaric, citric and malic acids on the residual SO₂ concentration in simulated used brine after pH adjustment and filtration is shown in Table 2. Residual SO₂ was substantially higher in brines containing citric and malic acids than in brine containing fumaric acid. Malic acid is the major acidic constituent of sweet cherries. (Marshall, 1954); fumaric and citric acids may be used as acidulants in dry mix brine formulations (Tennes et al., 1975). Measurements of calcium concentration in freshly prepared brines using titrimetric (Payne et al., 1969) and specific ion electrode (Orion) procedures provide further support for this hypothesis. For the latter procedure, the brine samples were diluted 1/100 and adjusted to pH 6 with KOH prior to analysis. The electrode responds to calcium activity rather than to concentration. In brine containing fumaric acid (Table 3), the electrode and titrimetric values for calcium concentration were similar and only slightly lower than the amount of calcium added to the brine. However, in brine containing citric acid, the calcium activity was less than half the concentration determined titrimetrically, indicating considerable chelation.

Other alkaline compounds might be used to neutralize waste (Table 4). Calcium hydroxide is more effective than sodium or ammonium hydroxides at pH 8 with respect to residual SO₂ concentration and cost. Calcium carbonate was not included in this comparison because it reacts very slowly with the brine. We have employed calcium hydroxide (lime) in all subsequent studies of sulfite precipitation.

The precipitated calcium sulfite and sulfate must be separated from the brine following neutralization. This may be done by filtration, centrifugation or sedimentation. We have examined the latter technique because of its simplicity. Data summarized in Table 5 show that a sludge of greater density (lower volume) will form more rapidly when the brine is neutralized slowly (10 min vs 2 min) and when the pH is adjusted to 8 rather than to 9. It is well known that the formation of a coarse precipitate is favored by slow addition of the precipitant. Following sedimentation, the supernatant and sludge can be separated for further treatment.

Disposal of supernatant and sludge

The supernatant and sludge both contain sufficient fermentable solids and residual sulfite or sulfate to yield objectionable odors when stored under anaerobic conditions (Table 6). This can be prevented by washing the sludge to remove fermentable solids. The washed sludge is similar in composition to the waste product of stack gas scrubbers used to remove SO₂ from power plant emissions and may be suitable for use as landfill (Anon. 1975). Weak brines and ponded plant effluents which contain sulfate rather than sulfite (due to oxidation during storage) will also yield an H₂S odor under anaerobic conditions, arising from the action of sulfate-reducing bacteria such as *Desulfovibrio* sp. This can be demonstrated by filtering the neutralized weak brine to remove calcium sulfate. The filtrate develops a yeasty odor after inoculation and incubation. However, the addition of synthetic calcium sulfate to the filtrate results in an H₂S odor. Weak brines, the supernatant resulting from brine neutraliza-

Table 1—Precipitation of CaSO₃ from waste cherry brine with Ca(OH)₂

Added Ca(OH) ₂ (g/L)	Brine pH	Filtrate SO ₂ (ppm)
0	3.52	4070
3.70	5.58	2140
4.74	6.10	1020
5.07	6.62	640
5.30	7.55	470
5.55	8.34	420
5.85	9.11	370

Table 2—Effect of organic acids on precipitation of CaSO₃ from simulated cherry brine

Acid	Filtrate SO ₂ (ppm)		
	pH 3	pH 8	pH 9
Fumaric (0.3%)	2230	150	80
Citric (0.3%)	2570	660	570
Malic (0.3%)	2280	290	290

Table 3—Ca⁺⁺ concentration in bisulfite brines containing fumaric and citric acids

Organic acid	Calcium concentration (M)		
	Electrode	Titrimetric	Added
Fumaric (0.32%)	0.16	0.17	0.19
Citric (0.39%)	0.07	0.16	0.18

Table 4—Comparison of CaSO₃ precipitants for waste brine

Precip- itant	Level of addition		Brine pH	Filtrate SO ₂ (ppm)	Cost ^{a,b}
	g/L	Meq/L			
None	—	—	3.4	4250	—
Ca(OH) ₂	5.60	151	8.0	400	0.75
NaOH	5.80	145	8.0	850	7.15
NH ₄ OH	14.80	260	8.0	950	5.40

^a Chemical Marketing Reporter, April 19, 1976

^b Cost in \$/1000 gal brine

Table 5—Sedimentation of CaSO₃ sludge in neutralized cherry brine

Lime addition time (min)	Adjusted brine pH	Sludge volume (ml)		
		2 min	5 min	10 min
2	8	82	51	34
	8.5	76	46	32
	9	85	66	48
10	8	72	12	12
	8.5	80	44	20
	9	76	49	36

tion and similar wastes containing sulfite or sulfate should not be stored under anaerobic conditions.

Such wastes might be disposed of by spray irrigation or by treatment in a municipal system, if available. Prior to disposal, low levels of SO_2 , not removed by precipitation, might be oxidized to sulfate with H_2O_2 (Table 7). This reaction is rapid and quantitative and might be used to obviate odor problems resulting from short-term handling and storage (Gerrish, 1974).

Deep well disposal has been investigated by the sweet cherry processing industry as an approach to bisulfite brine disposal (Sleder, 1975). This method is especially attractive in Michigan where municipal treatment may not be available and the use of spray irrigation may be limited by space and legal restrictions designed to limit the contamination of ground water with chloride. Cherry processing areas in this state are also in close proximity to abandoned deep wells. If strong brine were injected into a dolomite or limestone layer over a long period of time, one might expect a gradual loss in porosity near the bore hole due to the precipitation of calcium sulfite. In the laboratory strong brine can be neutralized with

CaCO_3 ; this is accompanied by a decrease in residual SO_2 as calcium sulfite precipitates (Table 8). Pretreatment of brine with lime followed by sedimentation, as described above, may prevent this reaction and extend the life of the well.

Chloride in waste brine

In some cases, the disposal of waste cherry processing brines may be complicated by the need to avoid groundwater pollution by chloride (from calcium chloride, an ingredient of dry mix brines). The removal of chloride from brine by chemical or physical means does not appear to be economically feasible. Consequently, research has focused on reformulating brine to eliminate chloride (Bedford, 1975). We have carried out some preliminary experiments with brines containing calcium dihydrogen phosphate in place of calcium chloride. While this compound performed well with respect to cherry firming and pH adjustment, it interfered with the precipitation of calcium sulfite from waste brine using $\text{Ca}(\text{OH})_2$ and other bases as precipitants. We also encountered a solubility problem with technical grade calcium dihydrogen phosphate, probably due to the presence of small amounts of dicalcium phosphate.

It might be more feasible to eliminate or reduce chloride in waste brine by returning to formulations prepared with gaseous SO_2 and CaCO_3 rather than by reformulating dry mix brines. The use of the older formulations might be made more attractive, especially for in-orchard brining, through the development of improved methods of brine preparation, handling and distribution. Such improvements might include automated brine make-up systems and tank truck delivery of brine to growers.

CONCLUSION

THE BISULFITE CONCENTRATION in waste cherry processing brine can be reduced to a level compatible with conventional disposal methods by neutralization with lime and separation of the precipitated calcium sulfite sludge. The extent of SO_2 removal will depend on the composition of the waste brine. Further reductions in sulfite can be achieved by oxidation with hydrogen peroxide.

Anaerobic storage of the sludge and liquid waste resulting from this treatment should be avoided to avert an odor problem.

The substitution of calcium dihydrogen phosphate for calcium chloride in dry mix brine formulations in order to eliminate chloride from processing wastes is not feasible.

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Table 6—Anaerobic fermentation of neutralized waste brine^a

Sample ^b	SO_2 (ppm)	Odor ^c
Sludge	—	H_2S
Washed sludge	—	None
Supernatant, strong brine	230	H_2S
Weak brine	25	H_2S
Filtrate, weak brine	35	Yeasty
Filtrate, weak brine + CaSO_4	35	H_2S

^a Adjusted to pH 7.5 with $\text{Ca}(\text{OH})_2$.

^b Inoculated with mixed culture (soil sample)

^c Incubated 4–5 days at room temperature

Table 7—Oxidation of residual SO_2 in liquid waste from neutralized brine using H_2O_2

H_2O_2 added (ml/L) ^a	Residual SO_2 (ppm)		Theor ^b
	5 min	60 min	
0	300	300	300
0.15	224	224	200
0.30	125	75	100
0.45	100	50	0

^a 31.8% H_2O_2

^b Based on stoichiometric relationship between SO_2 and H_2O_2

Table 8—Neutralization of waste brine with calcium carbonate^a

Holding time (hr)	Brine pH	Residual SO_2 (ppm)
0	3.43	4090
1	5.11	3310
3	5.36	2380
6	5.56	2100
18	6.02	549

^a 15g CaCO_3 /L brine

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Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.